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Methyl Parathion Persistence in Soil Following Simulated Spillage

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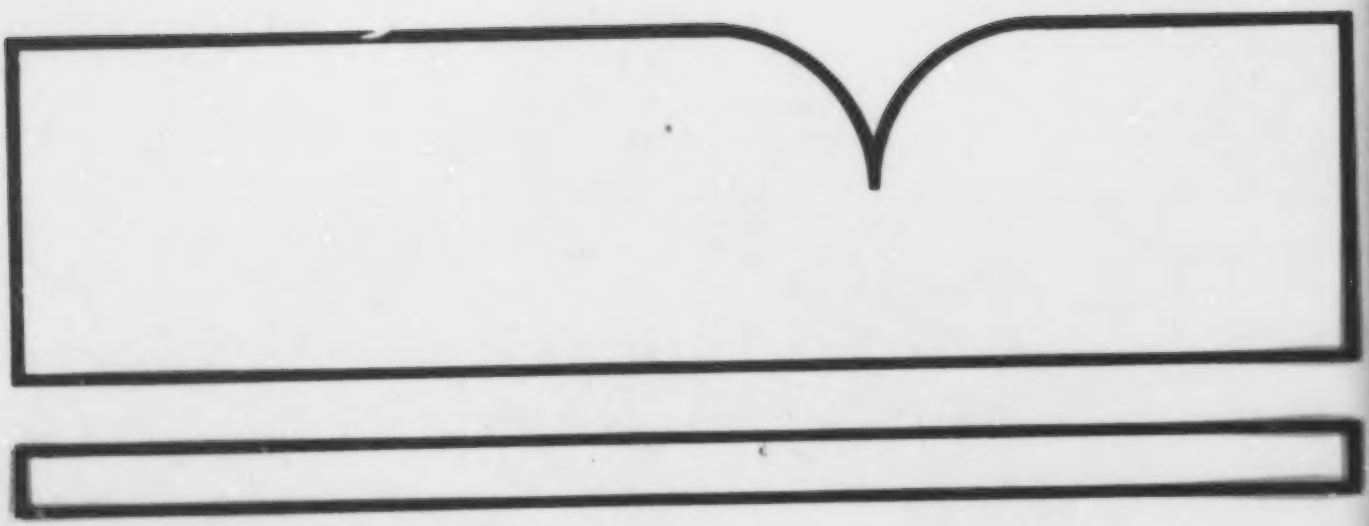

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16. ABSTRACT

Simulated spillage of emulsifiable concentrate (E.C) and microencapsulated formulations of methyl parathion on soil were studied. Persistence of residues from both formulations spilled as concentrates and as simulated drum rinses were followed for up to 45 months. Spillage of encapsulated formulation resulted in the formulation of a solid cake-like deposit on the soil surface, which could be a particularly attractive hazard to small children. At 45 months, soil residues had decreased by 64% for emulsifiable concentrate spills, and 68% for the soil beneath the microencapsulated cake. Residue in the cake itself only decreased by 31%. Soil residue levels from simulated drums rinses were essentially innocuous by 45 months for the emulsifiable concentrate and by one year for the microencapsulated material. The leching of methyl parathion from the microencapsulated cake into soil and the relationship between available residue and wet weather were investigated.

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Methyl Parathion Persistence in Soil Following Simulated Spillage

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Abstract. Simulated spillage of emulsifiable concentrate (E.C.) and microencapsulated formulations of methyl parathion on soil were studied. Persistence of residues from both formulations spilled as concentrates and as simulated drum rinses were followed for up to 45 months. Spillage of encapsulated formulation resulted in the formulation of a solid cake-like deposit on the soil surface, which could be a particularly attractive hazard to small children. At 45 months, soil residues had decreased by 64% for emulsifiable concentrate spills, and 68% for the soil beneath the microencapsulated cake. Residue in the cake itself only decreased by 31%. Soil residue levels from simulated drum rinses were essentially innocuous by 45 months for the emulsifiable concentrate and by one year for the microencapsulated material. The leaching of methyl parathion from the microencapsulated cake into soil and the relationship between available residue and wet weather were also investigated.

The banning, restricted use, and development of target insect resistance has, presumably, led to a rapid decrease in the use of persistent chlorinated hydrocarbon pesticides during the past six years. Although actual figures are well guarded in order "to avoid disclosure" (Fowler and Mahan 1978), it may be presumed that this decrease in use of relatively persistent materials has resulted in an increased use of organophosphorus and carbamate pesticides, which are generally considered to be less persistent, although they are often more acutely toxic. These latter two classes of pesticides are not considered to be excessively persistent in the environment since they are usually degraded quite rapidly when applied as dilute sprays for insect control. However, previous studies at this laboratory have found that spills of concentrated organophosphorus compounds such as parathion and azinphosmethyl persist in soil for many years, (Wolfe and Durham 1966; Wolfe *et al.* 1973; and Staiff *et al.* 1975). Such spills at ground sprayer fill sites, at aircraft application fill sites, near pesticide storage facilities, and beneath vehicles transporting leaking pesticide containers result in a persistent hazard to children, pets, farm animals, and wildlife.

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Methyl parathion (*O,O*-dimethyl *O-p*-nitrophenyl phosphorothioate) appeared to be one excellent substitute for the chlorinated hydrocarbon pesticides with regard to persistence in the environment. Its very rapid degradation after spraying, however, limits residual action towards target pests. This results in the need for excessive multiple spraying to achieve insect control. Residual action of methyl parathion has been improved by application of the material in a microencapsulated form. Microencapsulation not only increases the residual action, it also gives a significant decrease in acute oral and dermal toxicities (Cardarelli 1976).

The purpose of the present study was to determine the persistence of methyl parathion residues after simulated spills of emulsifiable concentrate and encapsulated formulations in order to assess the potential hazard of such spills. Simulated drum rinses of both formulations were also used to study persistence in a case where drum rinses were not added to the spray tank, as recommended, but were simply disposed of on soil near a fill site. The results apply not only to the potential hazard of concentrated spills, but also provide information that is applicable to waste disposal by burial and to the leaching of methyl parathion from microcapsules into soil.

Materials and Methods

Preparation and Treatment of Sampling Areas

Sampling areas were delineated by square sheet metal frames measuring 30 cm along each side and five cm deep. The frames were pressed into soil that had been well raked to remove large stones and to provide a relatively level surface. Approximately one-half of the frame was left above the soil surface so that more than one L of liquid could be added without overflowing the frame. The soil within the fenced plot assayed 6.0 to 10.2% clay, 26.0 to 29.0% silt, 60.0 to 67.3% sand, and 1.0 to 3.4% organic matter. This assay classifies the soil as sandy loam. The pH of the soil ranged from 6.6 to 7.8 with a mean of 7.2.

One L of the material was added to a frame resulting in a pool that filled the frame to a depth of approximately one cm before soaking into the soil. The materials added were (a) an undiluted emulsifiable concentrate (E.C.) methyl parathion formulation containing 51% active ingredient, (b) an undiluted encapsulated methyl parathion formulation containing 22% active ingredient, (c) a simulated drum rinse of the E.C. formulation produced by briefly swirling 60 ml of concentrate with 940 ml of water in a five gal (19 L) drum, and (d) a simulated drum rinse of the encapsulated formulation produced in the same manner as for (c). Each treatment was replicated in four frames and all frames were left in place for the duration of the study.

The sampling areas were subjected to the natural elements of the semiarid Pacific Northwest location. Rainfall averages approximately 25 cm per year, sunshine is prevalent for more than 275 days per year, and relatively high maximum temperatures occur with more than 31 days per year having temperatures above 32°C. The ground is normally covered with snow for approximately two months each year and the average daily temperature for the three months of winter is near 0°C.

Sampling and Extraction Procedures

Samples were taken one day after treatment and at appropriate intervals thereafter for 45 months. Cork borers, 20 mm in diameter, were used to obtain soil samples. A sample consisted of two cores obtained at different locations within a frame. Care was taken to avoid sampling the same area within a frame twice during the study. The cork borers were well cleaned between samples to avoid cross contamination. During dry periods the soil would not hold together in a core, so the sampling areas were watered with a sprinkler for three to four hours and then were allowed to partially dry prior to sampling.

The undiluted encapsulated formulation formed a thick "pancake batter" layer on the soil surface after the solvent had soaked into the soil. On drying, this layer of material hardened into a cake which, with aging, cracked and separated into smaller pieces. To sample this cake, pieces were broken off and any adhering soil was scraped away. Soil samples below the cake were obtained by removing a portion of the cake to uncover an area large enough to accommodate a cork borer. After obtaining a core sample, the cake was carefully replaced.

All soil and cake samples were air dried to a constant weight. Each soil sample was mixed and a weighed portion was ground in a mortar with anhydrous sodium sulfate. This mixture was then shaken with 100 ml of gas chromatographic grade benzene on a wrist-action shaker for 20 min. The extracts were filtered into amber sample bottles containing anhydrous sodium sulfate for storage pending analysis. A portion of each cake sample was weighed and ground in a mortar. The resulting powder was transferred to an amber sample bottle using 100 ml of gas chromatographic grade benzene. The resulting mixtures were shaken thoroughly by hand and anhydrous sodium sulfate was added before storage.

Analytical Details

Extracts were analyzed with a Varian Aerograph Model 1527C gas chromatograph, equipped with a 1975 detector oven update. Quantitation was accomplished with a Tracor flame photometric detector equipped with a 526 nm phosphorus filter. A 1.83 m × 3.6 mm stainless steel column packed with 1.5% OV-17/1.95% OV-210 on 100/120 mesh Chromasorb WHP was used. Inlet, column, and detector temperatures were 210, 200, and 225°C, respectively. For confirmation, all samples were chromatographed simultaneously in the same instrument using a 1.83 m × 6.3 mm glass column packed with 1.5% OV/17 on 100/120 mesh Chromasorb G and an alkali flame ionization detector. Operating temperatures were the same as used for the quantitative column.

Soil moisture measurements were made with a Wescor Psychrometrical microvoltmeter equipped with chromel-constantan thermocouples mounted in hollow porous ceramic bulbs (Wescor, Inc., 459 South Main St., Logan UT., 84321). After the 20 month sampling, the thermocouples were implanted in the soil and were left in place for the duration of the study. The thermocouple leads were protected from the elements with small plastic bags.

Results and Discussion

The persistence of methyl parathion in sandy loam soil following gross contamination by a simulated spill of an E.C. formulation is shown in Table 1. The initially high level of 48,900 ppm of pesticide in the soil decreased to 27,300 ppm in seven months and to 20,900 ppm after one year. Pesticide levels remained high during the rest of the study with 17,500 ppm present after 45 months. Apparent increases of residues after periods of wet weather, which are exhibited in Table 1 and in the following tables, will be discussed below.

The lowest lethal dose of methyl parathion reported for humans is five mg/kg (Fairchild 1977). This means that a one year old child ingesting contaminated soil from the simulated E.C. spill, assuming a body weight of ten kg, could conceivably receive a lethal dose of methyl parathion by eating only three g of soil that had been contaminated nearly four years earlier. This hypothetical case also assumes that all the residue that can be removed from the soil by our extraction procedure would also be removed in the digestive system. However, no data are available to support or refute this assumption.

The persistence of methyl parathion in soil contaminated by the simulated E.C. drum rinse is shown in Table 2. In this case, the initial residue was approximately equal to the 45 month residue found with the concentrate "spill" and would have the same potential for poisoning a child who ingested the soil.

Table 1. Persistence of methyl parathion in sandy loam soil following gross surface contamination with 51% emulsifiable concentrate formulation

Sampling time (months)	Date	Conditions	Pesticide contents of soil (ppm)[a]
			Sample depth 0-2.5 cm
0[b]	July 73	hot, dry	48,900 ± 3,600
1	Aug 73	hot, dry	33,700 ± 1,300
3	Oct 73	cool, dry	25,300 ± 1,700
7	Feb 74	cold, wet	27,300 ± 3,700
12	July 74	hot, dry	20,900 ± 1,100
14	Sept 74	hot, dry	20,800 ± 1,500
20	Mar 75	cool, wet	20,800 ± 1,000
26	Sept 75[c]	warm, wet	30,800 ± 1,100
33	Apr 76	cool, wet	37,800 ± 1,300
45	Apr 77[d]	cool, dry	17,500 ± 400

[a] Mean ± standard error for 4 replicates
[b] Initial sampling 1 day after treatment
[c] Wet conditions in Sept considered abnormal weather for this region
[d] Samples taken following an unusually dry winter with no snow cover

Table 2. Persistence of methyl parathion in sandy loam soil following contamination with dilute drum rinse of emulsifiable concentrate formulation

Sampling time (months)	Date	Conditions	Pesticide content of soil (ppm)[a]
			Sample depth 0-2.5 cm
0[b]	July 73	hot, dry	17,600 ± 900
1	Aug 73	hot, dry	10,800 ± 1,700
3	Oct 73	cool, dry	7,000 ± 860
7	Feb 74	cold, wet	8,000 ± 640
12	July 74	hot, dry	3,800 ± 390
14	Sept 74	hot, dry	2,000 ± 590
20	Mar 75	cool, wet	1,400 ± 240
26	Sept 75[c]	warm, wet	1,300 ± 540
33	Apr 76	cool, wet	1,400 ± 270
45	Apr 77[d]	cool, dry	130 ± 29

[a] Mean ± standard error for 4 replicates
[b] Initial sampling 1 day after treatment
[c] Wet conditions in Sept considered abnormal weather for this region
[d] Samples taken following an unusually dry winter with no snow cover

After one year 3,800 ppm still remained, but by 45 months the residue was only 130 ppm.

Table 3 shows the persistence of methyl parathion in the solid cake material which was formed when the concentrated microencapsulated formulation was "spilled". The initial residue contained 379,000 ppm and very high levels remained for the duration of the study with 262,000 ppm still remaining after 45 months. The cake apparently protects methyl parathion in the interior from

Table 3. Persistence of methyl parathion in solid cake material following gross surface contamination of soil with 22% microencapsulated formulation

Sampling time (months)	Date	Conditions	Pesticide content of a solid cake material (ppm)[a]
0[b]	July 73	hot, dry	379,000 ± 58,000
1	Aug 73	hot, dry	258,000 ± 63,000
3	Oct 73	cool, dry	305,000 ± 45,000
7	Feb 74	cold, wet	401,000 ± 80,000
12	July 74	hot, dry	87,500 ± 27,000
14	Sept 74	hot, dry	341,000 ± 82,000
20	Mar 75	cool, wet	149,000 ± 55,000
26	Sept 75[c]	warm, wet	492,000 ± 62,000
33	Apr 76	cool, wet	574,000 ± 42,000
45	Apr 77[d]	cool, dry	262,000 ± 22,000

[a] Mean ± standard error for 4 replicates
[b] Initial sampling 1 day after treatment
[c] Wet conditions in Sept considered abnormal for this region
[d] Samples taken following an unusually dry winter with no snow cover

degradation and volatilization, thereby aggravating persistence. The relatively large standard errors obtained probably reflect the different percentage of surface material included in different samples. The surface microcapsules contain less residue than the interior microcapsules, so the residue found will be a function of the ratio of surface microcapsules to interior microcapsules in the sample.

If the hypothetical child ate some of the cake material after 45 months, and assuming that the encapsulated form is nine times less toxic than the E.C. material (Cardarelli 1976), then the child would still have to ingest only about two g of cake to receive a potentially lethal dose. If a spill of encapsulated material is not properly cleaned up, the possibility of a child eating a piece of the resulting cake is not just a remote possibility. The cake has a very attractive sugary appearance when fresh and resembles maple sugar candy or broken cookies after some weathering has taken place.

Persistence of methyl parathion from simulated drum rinse with the encapsulated formulation is shown in Table 4. Even the initial residue of 2,140 ppm would not present a particularly great hazard to the hypothetical child, who would have to consume approximately 200 g of the contaminated soil to receive his lethal dose. By 32 months this residue had decreased to 1.15 ppm, which is probably harmless.

Another aspect of the study of the concentrated encapsulated methyl parathion "spill" was to characterize the leachability of methyl parathion from the microcapsules into the soil. This involved analysis of residues in soil obtained directly below the cake material (0 to 2.5 cm) and in soil at a greater depth (2.5 to 7.5 cm). The residues that were present in these layers are shown in Table 5. The large standard error values of Table 5 reflect the difficulty encountered in obtaining homogeneous samples. It is possible that when the encapsulated material was applied to the soil, some microcapsules were carried

Table 4. Persistence of methyl parathion in sandy loam soil following contamination with dilute drum rinse of microencapsulated formulation

Sampling time (months)	Date	Conditions	Pesticide content of soil (ppm)[a] Sample death 0-2.5 cm
0[b]	Aug 74	hot, dry	2,140 ± 210
1	Sept 74	warm, dry	940 ± 69
7	Mar 75	cool, wet	550 ± 180
13	Sept 75[c]	warm, wet	0.15 ± 0.06
20	Apr 76	cool, wet	230 ± 86
32	Apr 77[d]	cool, dry	1.15 ± 0.87

[a] Mean ± standard error for 4 replicates
[b] Initial sampling 1 day after treatment
[c] Wet conditions in Sept considered abnormal weather for this region
[d] Samples taken following an unusually dry winter with no snow cover

Table 5. Persistence of methyl parathion in sandy loam soil following gross surface contamination with 22% microencapsulated formulation

Sampling time (months)	Date	Conditions	Pesticide content of soil (ppm)[a] 0-2.5 cm	2.5-7.5 cm
0[b]	July 73	hot, dry	30,800 ± 8,400	3,700 ± 2,300
1	Aug 73	hot, dry	14,200 ± 1,800	1,490 ± 810
3	Oct 73	cool, dry	17,100 ± 2,800	1,190 ± 680
7	Feb 74	cold, wet	33,500 ± 7,500	1,590 ± 1,120
12	July 74	hot, dry	20,000 ± 8,100	1,030 ± 220
14	Sept 74	hot, dry	14,700 ± 4,700	602 ± 311
20	Mar 75	cool, wet	13,300 ± 3,300	891 ± 309
26	Sept 75[c]	warm, wet	8,500 ± 2,400	207 ± 92
33	Apr 76	cool, wet	5,300 ± 2,300	1,100 ± 89
45	Apr 77[d]	cool, dry	9,800 ± 5,200	578 ± 341

[a] Mean ± standard error for 4 replicates
[b] Initial sampling 1 day after treatment
[c] Wet conditions in Sept considered abnormal weather for this region
[d] Samples taken following an unusually dry winter with no snow cover

down into void channels in the soil giving a heterogeneous distribution throughout the sampling areas. It is also possible that even though the cake material was carefully removed before sampling the underlying soil, some microcapsules not attached to the cake existed as a heterogeneous layer over the soil surface and some of these were carried into the lower layer after the top layer was removed. Since residues present in the soil were very low with respect to residues in the microcapsules, contamination with even a small number of microcapsules would have resulted in erratic results.

Both layers of soil beneath the cake (Table 5) generally reflected the moisture dependent levels of residue found in the cake (Table 3). The residue

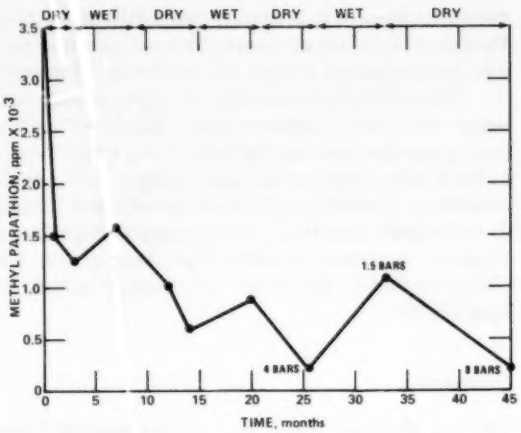

Fig. 1. Effect of soil moisture on the persistence of methyl parathion in sandy loam soil at 2.5 to 7.5 cm below gross surface contamination with 22% microencapsulated formulation

levels found in both layers appear to be a fairly constant percentage of the residue remaining in the cake. The residue in the upper layer remained approximately 6% of that in the cake and in the lower layer approximately 0.5% of that in the cake. This means that either the rate of transport of methyl parathion from the microcapsules down through the soil was equal to the rate of degradation in the soil or that the microcapsules were carried down into the soil during application and that the degradation of the methyl parathion they contained took place at the same rate as methyl parathion was lost from the surface cake.

The effect of seasonal climate on the apparent residues of methyl parathion in soil is shown in Figure 1, which illustrates the mean of residues found in the layer of soil from 2.5 to 7.5 cm below the simulated spill of encapsulated material. Spring sampling which usually follows cool, moist winters, often resulted in higher residues than were found the preceding fall after a hot, dry summer. This effect was not evident in the samples collected during April of 1977, because the areas were not sampled during the fall of 1976 and the winter of 1976/1977 was very dry. The effect of moisture on available residues is generally reflected in Tables 1 through 5.

The apparent lack of effect of moisture exhibited in Tables 1 through 4 and the 0-2.5 cm column of Table 5 for samples collected in March of 1975 are not really exceptions. These residue values were expected to be higher than those for the September 1974 samples since the March samples were collected following a cold wet winter; whereas the September samples were collected following a dry summer. However, the apparently low values for the March samples are surface residue values that reflect the effect of dry weather which occurred during early March. The March 1975 deeper soil samples shown in the 2.5 to 7.5 column of Table 5 exhibit the expected seasonal effect, because they had not yet lost the moisture collected during winter.

The effect of moisture on availability of residues was not postulated until after the Spring 1975 samples were analyzed. After that time, a soil psychrometer was employed to measure soil moisture during the last sample periods. Soil moisture values are included for the last three points in Figure 1. The

moisture present is inversely proportional to the psychrometer reading in bars. Periods of low soil moisture (26 to 45 months) gave low residue values while an intervening period of high soil moisture (33 months) gave higher residue values.

These observations concerning the effect of moisture on available residues agree with earlier observations (Davis *et al.* 1977) that available residues of both parathion and methyl parathion from "spills" on concrete surfaces were considerably higher after cool, damp weather than after hot, dry weather. It has also been reported that parathion becomes attached to active sites in soil prior to hydrolysis, and that water competes for these active sites (Yaron 1975). The observed increase of methyl parathion residues in moist soil may reflect competitive release, by water, of residues which have been bound but not yet hydrolyzed.

Summary

Spillage of either the E.C. or encapsulated formulations of methyl parathion may result in soil residue levels that present a toxic hazard for longer than four years. If drum rinses are dumped on the ground instead of into the sprayer tank, a toxic hazard may also be created. Spillage of concentrated encapsulated materials produces an especially attractive hazard for small children but the toxic potential of these spills can be greatly reduced by simple removal of the solidified cake. However, the soil below the cake should also be removed to eliminate all toxic hazard. The enhanced availability of residues during periods of wet weather may produce a seasonal increase in the toxic hazard at sites where spillage of concentrated organophosphorus pesticides have occurred.

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